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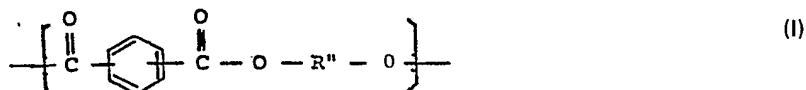
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(56) Documents cited
GB 1515585 EP A1 0067785
GB 1288361 US 4452962
GB 0816535 US 4348510
EP A1 0118388
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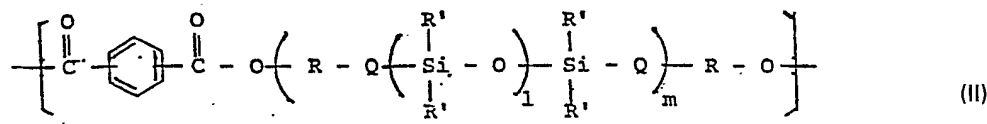
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C3T
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(54) Polyester-polysiloxane copolymers

(57) There is disclosed a polyester copolymer comprising, as the major structural units, repeating units of formula (I);



in which R'' is a lower alkylene radical,
and repeating units of formula (II);



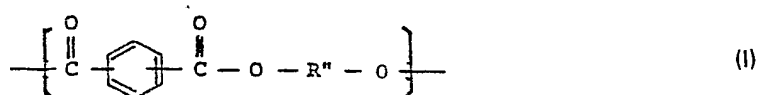
in which 1 is an integer of from 2 to 50, m is an integer of from 1 to 6, Q is an oxygen atom or a bond, R' is a hydrogen atom, a methyl group, or a phenyl group, and R is a divalent organic radical. The copolymerization ratio by weight of the repeating units of formula (I) to the repeating units of formula (II) is 40 - 99 : 60 - 1. The copolymers have a J-value of 10 - 300 ml/g. The suggested uses are for hoses, tubes, sealing materials and belts.

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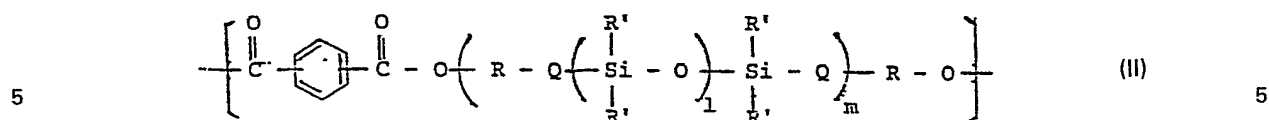
SPECIFICATION

Polyester-polysiloxane copolymers

- 5 The present invention is concerned with polyester-polysiloxane copolymers and their preparation. 5
 Resins or resinous mixtures containing a polysiloxane polymer have recently attracted much interest. It is generally known that polysiloxane polymers have excellent physico-chemical properties such as good resistance to extremes of temperature; they are put to practical use as primary products such as rubbers (silicone rubbers), oils and varnishes, and also as various secondary products prepared therefrom. Investigations are now being carried out in many technical fields with the object of finding new applications 10 for polysiloxane polymers which take advantage of the above physico-chemical properties. For example, in the field of engineering plastics, investigations to prepare tubes and hoses having a high shock resistance at low temperatures have been carried out to take advantage of the elasticity at low temperatures of polysiloxane polymers. In the field of medical products, the chemical stability of many polysiloxane polymers have already been put to practical use in orthopaedic materials, repairing materials for blood vessels, and bases for ointments. Polysiloxane polymers have also been used in the field of gas-separating membranes, with a view to economizing natural resources and energy. Such gas-separation applications include the separation and purification of recycled gases in the purification of helium, the separation of rare gases, the concentration of uranium, the enrichment of oxygen, and the synthesis of ethanol and of acetic acid. A polysiloxane membrane for the enrichment of oxygen is already used in practice to improve the fuel efficiency of boilers. 20
- The following processes are known for the preparation of resins or resinous mixtures containing polysiloxane polymers:
- (1) Kneading a polysiloxane polymer directly with another resin as described, for example, in Japanese Published Patent Specification 58-93749 and "Plastics World", March 1983, page 70; 25
 - (2) The preparation of block copolymers by chemically bonding polysiloxane polymers with another polymer such as a polyester, polyurethane, or polycarbonate, as described, for example, in Ann.N.Y. Acad. Sci., 146, 119 (1967) by W.L. Roff, J. Mom. Sci., 1, by W.J. Ward, and U.S. Patent 3,781,378;
 - (3) Graft copolymerizing polysiloxanes with a suitable backbone polymer, as described, for example, in Japanese Published Patent Specification 57-135007 and Collected Manuscripts for High Molecular Society 30 37, 461 (1982); and
 - (4) Synthesizing high molecular weight molecules by anionic polymerization of a polymerizing radical containing a poly-siloxane as substituent on the side chain, and described, for example, in Japanese Published Patent Specification 52-21021.
- 35 It is considered that of the above processes, the most suitable process with regard to ease of molecular designing to make resins or resinous mixtures which exhibit their mechanical, electrical and physical properties to best advantage in accordance with their proposed use is process (2) above in which a block copolymer is obtained by chemically bonding a polysiloxane polymer with another polymer.
- It is known that polyester resins obtained from a dicarboxylic acid and a glycol have excellent mechanical properties, heat resistance, and abrasion resistance, and many are widely used in domestic or industrial instruments or apparatus, electronic parts, and automobile parts. For use in automobile parts, however, a low temperature flexibility superior to that of ordinary polyester resins is preferred. Polyester elastomers in which a polyether is used in their preparation instead of a glycol are therefor widely used for such applications.
- 45 Such polyester-polyether copolymers have, however, a defect in that their properties are significantly affected at low temperatures such as from 0°C to -40°C. 45
- Moreover, their oil resistance is inferior because of the polyether component used and their resistance to hydrolysis is poor because of the ester linkages.
- The object of the present invention is to provide resins free from these defects and, more particularly, to provide a group of novel aromatic polyester resins having a polyorganosiloxane component which achieve this object. 50
- The present invention is essentially concerned with certain novel aromatic polyester-polyorganosiloxane copolymers which have better properties, particularly with respect to the aspects just mentioned, than the polyester-polyether copolymers described above. Although the polymers of the present invention are novel, it has been proposed in U. S. Patent 3,935,154 to prepare a polymer suitable for use as a mould release agent or as a level extending agent by incorporating a poly-organosiloxane component in an aliphatic polyester chain and in U. S. Patent 4,348,510 to prepare a polymer having improved fixing and blocking properties by reacting a minor amount of a polyorganosiloxane component having a polyoxy alkylene chain at both ends with an aromatic polyester rich in diol.
- 60 According to the present invention, there is provided a polyester copolymer comprising, as the major structural units, repeating units of formula (I); 60



in which R'' is a lower alkylene radical, and repeating units of formula (II);



in which 1 is an integer of from 2 to 50, m is an integer of from 1 to 6, Q is an oxygen atom or a bond R' is a hydrogen atom, a methyl group, or a phenyl group, and R is a divalent organic radical, and having a J-value of 10 - 300 ml/g, the copolymerization ratio by weight of the repeating units of formula (I) to the repeating units of formula (II) being 40 - 99 : 60 - 1.

These copolymers have the good properties, such as heat resistance, water absorption resistance, hydrolysis resistance, and chemical resistance, associated with polyorganosiloxanes, while retaining the good properties characteristic of polyesters. They are therefore well suited for the production of hoses, tubes, sealing materials, such as gaskets and packings, and belts, such as caterpillar tracks and fanbelts.

In the copolymer of the present invention, the relative amounts of units of formula (I) and units of formula (II) are such that units of formula (I) constitute about 40 - 99 % by weight and units of formula (II) constitute about 60 - 1 % by weight of the total amount of both units. When the amount of units of formula (I) is less than 40 % by weight, the characteristic properties inherent in polyesters are affected and the J-value of the copolymer becomes very low. On the other hand, when the amount of units of formula (I) exceeds 99 % by weight, the amount of polyorganosiloxane units of formula (II) is too small and the characteristic properties inherent in polyorganosiloxanes, such as low temperature flexibility, heat resistance, hydrolysis resistance, and chemical resistance, are significantly reduced. A ratio by weight of unit (I): unit (II) of 50 - 97% : 50 - 3 % is preferred.

The polyester copolymers of the present invention have a J-value of 10 - 300 ml/g, preferably 20 - 250 ml/g. The J-value (ml/g) is an index for evaluating the solution viscosity of a polymer, which indirectly provides the molecular weights (MW) of the copolymers of the present invention.

The J-values were determined according to the following method: (Deutsche Industrienorm (DIN) 16779 Teil 2) : in a measuring flask of 50 ml volume, 0.25g of a sample was weight accurately and the sample was dissolved in a mixed solvent consisting of: phenol/o-dichlorobenzene (1:1 by volume) at room temperature or at an elevated temperature; the whole volume was adjusted to 50 ml at 25°C. The dropping times of the solution and the solvent were then measured at 25°C using a viscometer of the Uberode type. J-values are calculated according to the following equation:

$$\text{J-value} = \frac{(\text{dropping time solution/dropping time of solvent}) - 1}{\text{concentration of the sample (5mg/ml)}} \text{ ml/g}$$

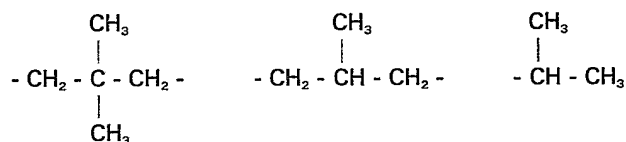
$$\eta_{\text{rel}} (\text{relative viscosity}) = \frac{\text{dropping time of solution}}{\text{dropping time of solvent}}$$

The J-values of the copolymers can be adjusted as required by varying the amount of esterification catalyst or the esterification time, or by the addition of a third monofunctional component (as described hereinafter).

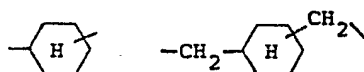
Suitable aromatic dicarboxylic acid residues in units (I) and (II) of the present invention include for example, terephthalic acid and/or isophthalic acid. Preferably 100 - 20% of terephthalic acid residues and 0 - 20% of isophthalic acid residues are present.

Suitable R'' groups in unit (I) of the present invention include, for example, lower alkylene radicals, especially alkylene radicals having 2-4 carbon atoms, which can be branched. Particularly preferred are dimethylene and tetramethylene residues.

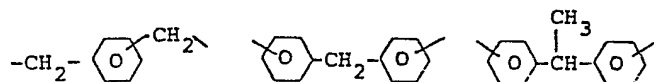
The R group in unit (II) of the present invention is a divalent organic radical, such as an alkylene radical, which can be branched, polyoxyethylene residue comprising 1-4 oxyethylene units, a divalent alicyclic radical, or a divalent aromatic radical. (A divalent alicyclic radical is defined as a divalent radical containing at least one alicyclic hydrocarbon residue and a divalent aromatic radical as a divalent radical containing at least one aryl group.) As the divalent alkylene radical, a straight chain or branched chain alkylene radical of C₂ - C₂₀ is preferred. Suitable branched alkylene radicals include for example, groups of the formulae



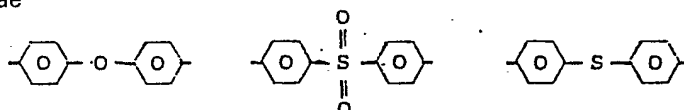
Suitable divalent alicyclic radicals include, for example, groups of the formulae



which may be substituted further by lower alkyl group(s). Suitable divalent aromatic radicals include, for example, groups of the formulae



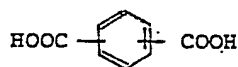
which may also be substituted further by lower alkyl group(s). The divalent aromatic radical can contain an ether linkage, a sulphonyl linkage, a sulphide linkage, or a carbonate linkage, as exemplified by groups of the formulae



In each of the radicals described above, the hydrogen atom(s) can be replaced by halogen atom(s).

On the other hand, R' in unit (II) of the present invention is a hydrogen atom, a methyl group, or a phenyl group. Although the radicals R' are usually the same, they can be different from each other.

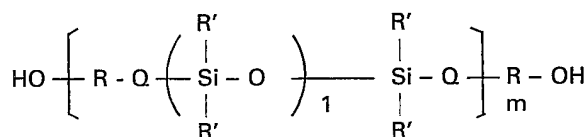
The polyester copolymers of the present invention, are usually prepared by polymerizing (i) a phthalic acid of the formula (III):



or an alkyl (C₁ - C₄ ester thereof, (ii) a diol constituent of the formula (IV):



in which R'' has the same meaning as above, and (iii) a polyorganosiloxane diol of the formula (V):



in which each symbol has the same meaning as above, by an esterification reaction.

The method of polymerization generally employed is a process in which the components of formulae (III), (IV) and (V) are copolymerised in one reaction by subjecting them to esterifying conditions (one step method). Specifically, the high molecular weight polyester copolymers of the present invention can be obtained, for example, by mixing an aromatic dicarboxylic acid of formula (III), such as terephthalic acid and/or isophthalic acid, a diol of formula (IV), such as ethylene glycol or 1,4-butanediol, and a polyorganosiloxane of formula (V) or terminal diol type, reacting the three components with each other by heating the mixture at 170 - 280°C in an inert gas current under atmospheric pressure in the presence of an esterification catalyst, then effecting polycondensation by heating at 200 - 280°C under a reduced pressure of 30mm Hg or less, preferably of 15mm Hg or less, and further effecting polycondensation by heating at 220 - 280°C under high vacuum (for example, of 1mm Hg or less, preferably, 0.1 mm Hg or less).

In practice, it is preferably to effect such a polymerization reaction using almost equimolar amounts of the three components. Further, it is preferable to use the diol (IV) and the polyorganosiloxane diol (V) in a weight ratio of 40 - 99 : 60 - 99 in order to achieve the desired copolymerization ratio of unit (I) : unit (II) in the resulting copolymer.

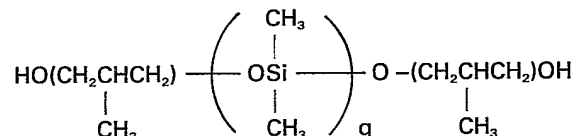
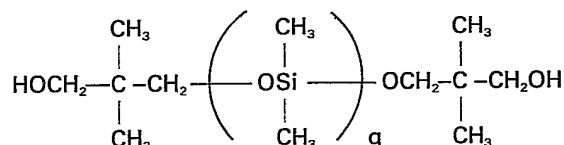
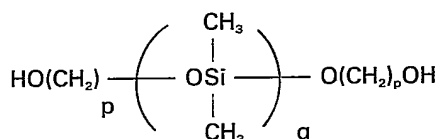
Suitable esterification catalysts for forming the ester linkages, of the copolymers include, for example one or more catalysts of tin, titanium, or lead. Preferred catalysts are dialkyl tin oxides such as dibutyl tin oxide and dioctyl tin oxide, dialkyl tin alkylates such as dibutyl tin laurylate and dibutyl tin bis(2-ethylhexanoate), tetraalkyl titanates such as tetramethyl titanate, tetrabutyl titanate, and tetraisopropyl titanate, titanium oxalates such as titanium potassium oxalate, and lead compounds such as lead acetate. It is particularly preferred to use at least one titanium catalyst, such as a tetraalkyl titanate or a titanium oxalate, in order to obtain good results.

The polyester copolymers obtained are mainly straight chain copolymers resulting from a substantially equimolar reaction of the diol (IV), the polyorganosiloxane diol (V), and the phthalic acid (III), in which the units (I) and (II) are bonded randomly.

The polyester copolymers of the present invention can also be obtained by first preparing prepolymers

containing the units (I) and/or (II) which have a carboxyl group or a lower alkylester at one terminal and a hydroxyl group at the other terminal, and then polymerizing them under esterfying conditions (two step method). The polyester copolymers obtained by such a method have the units (I) and/or (II) bonded in blocks.

- 5 Suitable starting compounds of the formula (V) are those available under such names as diol-terminated polyorganosiloxanes, dihydroxy-terminated polyorganosiloxanes, silicone diols or modifications thereof. Preferred examples are compounds of the following formulae:



25 in which p is an integer of 2,4 or 10 and q is an integer. 30

The polyester copolymers of the present invention have excellent low temperature flexibility flexibility at temperatures of 0 to -40°C because of their low T_g (glass transition temperature) which is a property characteristic of polyorganosiloxanes; they also have very excellent hydrolysis resistance because of the superior water resistance of the polyorganosiloxane components which act as soft segments, regardless of the fact that the polymers are formed by ester linkages.

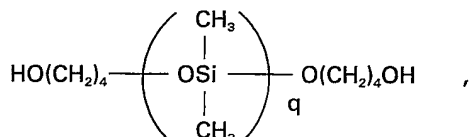
It is necessary that the copolymers of the present invention comprise as the major constitutional units the units (I) and/or (II). Provided that this essential requirement is satisfied, the copolymers of the invention can contain a third unit in their polymer chain. Suitable additional components to provide the third unit include, for example, various dicarboxylic acids, diols and oxycarboxylic acids which are capable of being copolymerized into a straight chain by ester linkages. It is desirable on copolymerizing in the presence of the additional component to adjust the amount of the whole dicarboxylic acid components so that it is equimolar to the amount of the whole diol components. Further, it is usually satisfactory to adjust the amount of the third unit to within 50 mol% of the whole of the structural units. Preferred compounds for providing the third unit are aromatic dicarboxylic acids other than phthalic acid, aliphatic dicarboxylic acids such as oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid and dodecane dicarboxylic acid, alicyclic dicarboxylic acids such as hexahydroterephthalic acid, decalin dicarboxylic acid, and tetralin dicarboxylic acid, hydroxy acids such as glycolic acid, oxybenzoic acid, alicyclic diols such as cyclohexane dimethanol and tricyclodecane dimethylol, and aromatic diols such as bisphenol A, bisphenol S, bis-hydroxyethoxy bisphenol A, and tetrabromo bisphenol A. Carboxylic acids other than dicarboxylic acids and alcohols other than diols may also be used. For example, polyfunctional compounds such as trimellitic acid, trimesic acid, pyromellitic acid, tricarballic acid, trimethylol-propane, glycerin and pentaerythritol, and monofunctional compounds such as benzoic acid, naphthoic acid, stearyl alcohol, palmitic acid and their derivatives can be used. The polyfunctional compounds can be used in such amounts that the polyesters formed are substantially linear; the monofunctional compounds can be used to adjust the molecular weight of the resulting copolymer.

In addition, the polyester copolymers of the present invention can also contain those additives usually added to polyesters, for example, thermal stabilizing agents such as phosphorus, antioxidants such as hindered phenols, ultraviolet absorbing agents such as benzotriazole, hydroxybenzophenone, and cyanoacrylate, pigments and dyestuffs such as titanium oxide, carbon black, and tetrazole blue, nucleating agents such as talc, crystallizing agents such as higher fatty acid salts, and mould releasing agents.

In order that the invention may be more fully understood, the following examples are given by way of illustration.

Example 1

In a cylindrical flask of 1ℓ volume were placed 29.15g (0.15 mol) of dimethyl terephthalate, 1.35g (5% by weight of the whole diol components) of dibutanoloxy-terminated polydimethylsiloxane having an average molecular weight of 1247, which is represented by the formula



where q is an integer, and 25.65g of 1,4-butanediol; 0.9g of an isopropanol solution (10%) of isopropyl titanate ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) was then added as catalyst. The mixture was stirred for 3 hours at 180°C (in a metal bath) while introducing nitrogen gas. The temperature of the metal bath was then raised by 70°C to 250°C and the pressure was reduced to 15mm Hg by means of a tap aspirator for a period of 30 minutes. The heating was continued for one hour at 250°C while stirring under the reduced pressure. The pressure was then reduced further to 0.05mm Hg or less using a high vacuum pump and stirring was continued for a further hour at 250°C. The product was removed under a nitrogen atmosphere as a white, highly viscous polymer.

The J-value of the polymer was 99, as determined at 25°C using phenol/*o*-chlorobenzene (1:1 by volume) as the solvent. The infrared absorption spectrum of the polymer showed absorptions characteristic of polydimethylsiloxanes at 800 and 1000-1100 cm^{-1} , though they were weak. The ^1H -NMR spectrum of the polymer showed an absorption due to the methyl groups bonded to the silyl group of polydimethylsiloxanes at 0.1 ppm.

From these results, the polymer was consistent with a copolymer of polyester and polydimethylsiloxane. by means of DSC (Mettler TA-2000 type and Perkin-Elmer 2C type), the polymer was found to have a Tg of 54°C and a Tm (melting point) of 223°C.

Examples 2 - 6

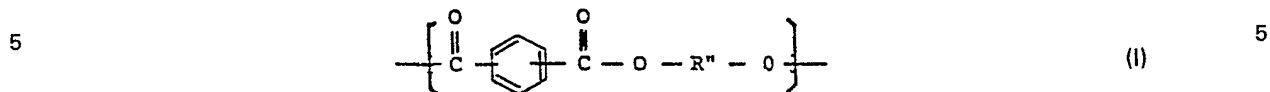
Various polyester copolymers were prepared in the same manner as Example 1. The starting materials used and the properties of the copolymers obtained are shown in Table 1.

TABLE 1

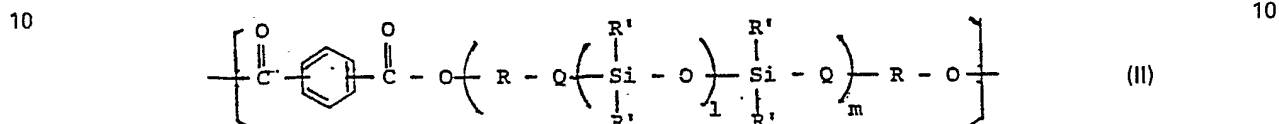
Phthalic acid constituent Formula (III)	Example 2	Example 3	Example 4	Example 5	Example 6
	Dimethyl terephthalate 29.15g (0.15 mol)	The same as Example 2	The same as Example 2	The same as Example 2	Dimethyl phthalate 24.24g (90 mol %) + Isophthalic acid 2.50g (10 mol %)
Organo-siloxane constituent	Dibutanoloxy-terminated polydimethyl siloxane (Mw = 907) 2.72g (10 wt % of the whole diol)	$\text{HOCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\left(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OSi}(\text{CH}_3)_2\right)_q\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ (Mw = 613) 2.71g (10 wt % of the whole diol)	Dibutanoloxy-terminated polydimethyl siloxane (Mw = 719) 2.17g (8 wt % of the whole diol)	Dibutanoloxy-terminated tetramethylsiloxane $\text{HO}(\text{CH}_2)_4\left(\text{CH}_3\right)_2\text{OSi}\left(\text{CH}_3\right)_2\text{O}(\text{CH}_2)_4\text{OH}$ (Mw = 310) 4.06g (15 wt % of the whole diol)	Dibutanoloxy-terminated polydimethyl siloxane (Mw = 719) 2.69g (10 wt % of the whole diol)
Diol constituent Formula (IV)	1,4-Butane-diol 24.34g (90 wt % of the whole diol)	The same as Example 2	1,4-Butane-diol 24.88g (92wt % of the whole diol)	1,4-Butanediol 22.99g (85 wt % of the whole diol)	1,4-Butane-diol 24.35g (90 wt % of the whole diol)
Catalyst	Ti(O-C ₃ H ₇) ₄ 0.09g				
Properties ¹ H-NMR	Signal of the methyl groups bonded to the silyl group at 0.1 ppm				
J-value	110	84	95	74	85

CLAIMS

1. A polyester copolymer comprising, as the major structural units, repeating units of formula (I);



in which R'' is a lower alkylene radical, and repeating units of formula (II);



- 15 in which 1 is an integer of from 2 to 50, m is an integer of from 1 to 6, Q is oxygen atom or a bond, R' is a hydrogen atom, a methyl group, or a phenyl group, and R is a divalent organic radical, and having a J-value of 10 - 300 ml/g, the copolymerization ratio of weight of the repeating units of formula (I) to the repeating units of formula (II) being 40 - 99 : 60 - 1. 15
- 20 2. A copolymer according to claim 1, in which R in the formula (II) is a C₂ - C₂₀ alkylene radical which can be branched, a polyoxyethylene radical containing 1 - 4 oxyethylene units, a divalent alicyclic radical, or a divalent aromatic radical which can contain an ether linkage, a sulphonyl linkage, a sulphide linkage or a carbonate linkage, in which the hydrogen atom(s) in any of said radicals can be optionally replaced by halogen atom(s). 20
- 25 3. A copolymer according to claim 1, in which the aromatic dicarboxylic acid residues in the repeating units of formulae (I) and (II) comprise 100 - 20% of terephthalic acid residues and 0 - 80% of isophthalic acid residues. 25
4. A copolymer according to claim 1, in which the repeating units of formula (I) and the repeating units of formula (II) are present in the polymer chain in blocks and/or at random.
- 30 5. A polyester-polysiloxane copolymer substantially as described herein with reference to the Examples. 30

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copolymers
PUBN-DATE: August 13, 1986

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APPL-DATE: January 30, 1986



PRIORITY-DATA: JP01914285A (February 1, 1985)

INT-CL (IPC): C08G077/48

EUR-CL (EPC): C08G077/50 , C08G077/445

US-CL-CURRENT: 528/26

ABSTRACT:

CHG DATE=19990617 STATUS=O> There is disclosed a polyester copolymer comprising, as the major structural units, repeating units of formula (I);  in which R' is a lower alkylene radical, and repeating units of formula (II);  in which l is an integer of from 2 to 50, m is an integer of from 1 to 6, Q is an oxygen atom or a bond, R' is a hydrogen atom, a methyl group, or a phenyl group, and R is a divalent organic radical. The copolymerization ratio by weight of the repeating units of formula (I) to the repeating units of formula (II) is 40-99 : 60-1. The copolymers have a J-value of 10-300 ml/g. The suggested uses are for hoses, tubes, sealing materials and belts.